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A Study of the Relative Effectiveness

of Four Insolubilizing Agents in

Starch-Latex and Protein-Latex Coatings

by

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in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

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Abstract:

    The process of offset lithography requires several unique
characteristics in paper. One of these is an ability in the sheet
surface to accept water without deteriorating. Offset coatings
commonly use starch and protein in their binder systems. These
adhesives are inherently water sensitive. The characteristic of
water resistance in coated grades can be obtained through the use
of crosslinking agents. Among the more commonly used are urea-
formaldehyde, melamine-formaldehyde, and glyoxal. A more recent
development involves the use of ammonium zirconium carbonate.

    Through the years many studies have examined the effects of
various insolubilizing agents in starch coatings. Most of these
have analyzed only one agent and have all but excluded protein coat-
ings. A need seemed to exist for a comparative analysis of the
commonly used insolubilizing agents in both starch and protein coat-
ings. The lack of literature concerning ammonium zirconium carbonate
suggested that its analysis should also be included.

    A series of starch and protein based coatings were prepared
using 16 parts adhesive and 100 parts clay. Styrene-butadiene latex
was included in both coatings. Urea-formaldehyde, melamine-formalde-
hyde, and glyoxal were added at levels of 5, 7, 9, 11, and 13 percent
based on dry starch or protein. Ammonium zirconium carbonate, due
to its purported superior insolubilizing efficiency was added at
levels of 1, 3, 5, 7, and 9 percent. A four pound coat weight was
applied by a hand-held blade drawdown technique to a 45 pound base
sheet.

    Testing of water resistance was carried out via an on-press
technique. The samples were allowed to cure two months before
testing. Results showed that urea-formaldehyde produced the highest
degree of water resistance. Ammonium zirconium carbonate was compet-
itive with UF and MF resins when added at levels greater than 5 %,
even when those agents were added at higher levels. Glyoxal harmed
starch-latex coating water resistance. Analysis of the protein-
latex coatings proved inconclusive.

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Introduction:

Papers used for lithography require several characteristics to permit acceptable printing. The process of offset lithography involves the transfer of an image to a rubber blanket from a planographic plate. Seperation of the image and non-image areas is maintained through the mutual repellancy of ink and water. The image is delivered to the paper from the rubber blanket. One of the most important requirements of paper for this process is a resistance to wet abrasion and picking. These characteristics can be obtained in starch and protein based coatings through the addition of various crosslinking agents. These agents in effect water proof the coating. Among the more commonly used are urea-formaldehyde, melamine-formaldehyde, and glyoxal. A recent development which has been poorly substantiated in the literature is ammonium zirconium carbonate.

Through the years the literature has reported many studies concerning the use of urea-formaldehyde, melamine-formaldehyde, and glyoxal to insolubilize starch coatings. The use of ammonium zirconium carbonate has been discussed in several patents. Very little work is available comparing these agents when used with protein. The literature also seems deficient in comparing the relative effectiveness of these agents under typical offset coating conditions. This thesis is meant to provide such a study. It will examine the use of urea-formaldehyde, melamine-formaldehyde, glyoxal, and ammonium zirconium carbonate, as crosslinking agents for the improvement of water resistance in starch and protein based coatings.

Theoretical Discussion:

Surface Strength of Coated Papers:

A significant problem encountered in offset lithography is that of insufficient paper surface strength. It is manifested by a release of fibrous materials from uncoated sheets and by coating particles from coated papers. These phenomena are referred to as

linting and picking. Both are of major concern to printers and
paper makers since they contribute to a degradation in print quality.
The material released by the paper surface tends to accumulate on
the blanket and plate, eventually working its way into the ink and
water distribution systems. Three problem phases are easily recog-
nized. The initial phase is the pickout. Coating released from the
image area leaves a noticeable defect in the finished product. The
second phase is that of repeating defects, "hickies." They are caused
by a build up on the plate or blanket resulting in localized poor
ink transfer. These defects are seen in each successive sheet.
The final phase occurs when released material works its way into the
ink and water distribution systems. It results in an upset of the
normal ink-water balance.[1]

The surface strength of offset lithographic papers is signif-
icantly affected by the water requirement of the process. This is
particularly true of coated grades. Since lithography is based on
the mutual repellancy of ink and water, when the image is delivered
to the sheet, the non-image area will receive a thin film of water.
This water has a chance to soften the coating. In multi-color
printing operations the softened coating may fail in subsequent
applications due to the strong tack force of the ink. In practice
the ink and water are not completely immiscible. After the press
has stabilized, droplets of fountain solution become entrained in
the ink. The end result is that the ink may in fact transfer three
times as much water to the sheet as the non-image area.[2]

The ammount of water transferred to the sheet during the printing
process is dependent on several variables. It directly influences
the quantity of coating removed. Among the variables involved in
water transfer are contact time between the sheet and impression
blanket, ink density, and the grain size of the plate. The contact
time is a complex combination of the printing cylinder diameter,
press speed, impression used, and to a lesser extent the ink tack
and paper resiliency. The effect of ink on water transfer has al-
ready been mentioned. Ultimately it is the plate that will control

the maximum water transfer. It is the plate which picks up water from the fountain. A more grainy plate will transfer more water. According to Beckman[2] under average operating conditions the contact time is expected to be in the range of 3 to 10 msec. With a medium grain plate and 10 msec contact time the non-image area water film thickness will be approximately 15 microns. This ammounts to 0.10 lb/ream (25 x 38 - 500) in the non-image area. Total water transfer may be three times this much.

Acceptable quality printing requires that the water applied to the sheet surface must be quickly absorbed by the sheet. If the water is not absorbed by the sheet it will present a barrier to good ink transfer in later stages. A condition called scumming is the result. Solid image areas may become weak and gray. At the same time the water and ink vehicle are absorbed by the paper, the ink pigment must be left on the surface. A unique set of characteristics is required. While water is being drawn into the sheet from the surface so as not to interfere with ink deposition it must not soften the coating. These requirements have led to the use of various insolubilizing techniques to prevent the coating from softening.[3]

Use of Insolubilizing Agents:

Historically, casein and more recently protein adhesives have dominated the offset coating industry. They are the easiest of the natural adhesives to insolubilize. Casein shortages during World War II started the industry looking for a substitute. The availability of starches with rheological properties superior to proteins has shifted the emphasis of the industry. Starches also have economic advantages. The major disadvantage of starch adhesives remains their inherently poor water resistance. The increase in press size and speed coupled with an increased need for inexpensively produced offset publications has further increased the cost advantage of using starches. This has led to much work in the area of improving the water resistance of starch coatings.

Both starch and protein coatings usually require some sort of insolubilizing agent to improve their water resistance. Several groups of compounds have gained prominence in this field. Among the more commonly used are urea-formaldehyde, melamine-formaldehyde, and glyoxal. A more recent development concerns the use of ammonium zirconium carbonate.

Urea-Formaldehyde:

Urea-formaldehyde resins have been used extensively to improve the water resistance of coatings. Numerous patents exist covering its use.[4-6] Its properties have been widely discussed in the literature.[7-11] It is generally accepted that urea-formaldehyde increases water resistance via a combination of blocking and cross-linking reactions. Cleek and Chase[9] have shown that while water resistance can be improved by the use of urea-formaldehyde, moisture vapor transmission is left unhindered. Their work indicates that a continuous film is not being formed. This is essential for use in offset lithography. If a continuous film is produced the water transferred to the sheet surface cannot be dissipated and will present a barrier to ink transfer in the next application.

Urea-formaldehyde is commonly used in starch coatings. Several types are available including dimetholyol urea, urea-formaldehyde concentrates and resin polymers. These latter are available with varying formaldehyde to urea ratios. In reactions with starch, the accepted mechanism involves a methylol group on the resin combining with a hydroxyl on the starch (α-glucoside). A water molecule is split off. The reaction is shown in Figure 1. The reaction of one urea-formaldehyde polymer with more than one starch chain establishes a crosslinked network. Reduced solubility of the starch is explained through two mechanisms. First, large agglomerates are formed by the crosslinking action. It is commonly known that large polymeric systems are much less soluble. Second, the hydroxyl sites active in hydrogen bonding with water are effectively blocked. With the water inter-action sites blocked the starch is rendered much less soluble.[10]

Reaction of Starch with Urea-Formaldehyde

Figure 1

```
      H                H    O    H
R--COH      +    HOC--N--C--N--COH   ───────>
      H                H    H       H    H

Starch              Urea-Formaldehyde
```

```
                     H    H    O         H
              R--C-O-C--N--C--N--COH      +      H2O
                     H    H    H       H    H

                   Starch  UF  product
```

```
         H    O    H                H
2  HOC--N--C--N--COH   ──────>     CO   +   H2O   +
         H    H       H    H                H

     UF  Resin
```

```
       H    O    H    O    H
HOC--N--C--N--C--N--C--N--COH
       H    H       H    H    H       H    H

   Crosslinked  UF  Resin  Product
```
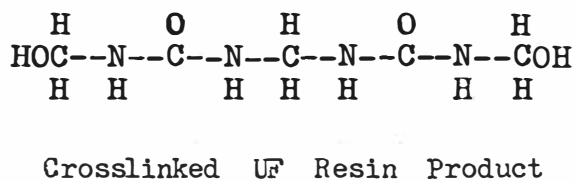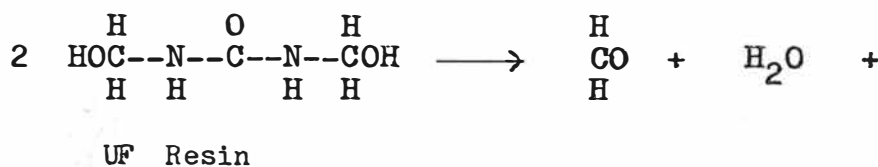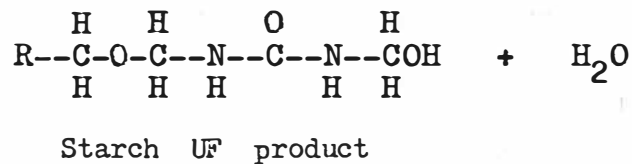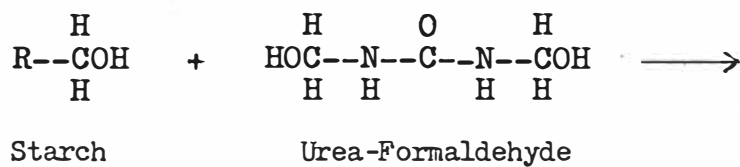
Urea-formaldehyde has been used over a broad range of addition levels in starch coatings. Addition levels are selected based on the degree of water resistance desired, the resin concentration, and the ratio of formaldehyde to urea. To achieve a higher degree of water resistance more crosslinking and blockage of hydroxyl sites is required. Accomplishing this requires higher addition levels. Economics enter into the equation as addition levels become higher. At some point it may become more cost effective to use an inherently less soluble adhesive. The consideration of resin concentration is simply one of increasing the active ingredient per measure of addition. The formaldehyde-urea ratio is varied to assure the proper concentration of each reactant in forming and maintaining the desired condensation product. Belche and Cleek[7] have found a molar ratio of 2 to 1 formaldehyde to urea to be optimum.

Urea-formaldehyde resins do not impart immediate water resistance to the coated surface. The resin requires a curing period to develop maximum resistance. The length of cure is dependant on several factors. The most important is the pH of the coating formula. For optimum results a pH range of 3 to 4 is suggested. Above this pH curing is slow. Below this range the resin becomes too active and may gel. Since it is usually desireable to run a coating color near neutral conditions, the pH requirement for resin curing is met through the use of catalysts. The two most widely recognized categories for use with urea-formaldehyde are ammonium salts of strong acids and aluminum salts. The aluminum salts are preferred because of their ease of use and more powerful catalytic effect. Heat and resin concentration also influence the rate of cure. Higher temperatures increase the cure rate. Higher concentrations reduce cure time.[12]

Urea-formaldehyde resins also find application in protein based coatings. (Casein will be considered as a protein. In general its reactions and properties are similar to soya protein.) Low addition levels (2-4 % based on the weight of protein) are usually

required to avoid severe viscosity increases. Ritson[3] states that these increases may be caused by the interaction of protein and the free formaldehyde present in urea-formaldehyde resins.

The insolubilization of protein is similar to that of starch. It is thought to occur through a reaction of methylol groups with active hydrogen atoms on the protein molecule. The same combination of crosslinking and blocking are postulated as the reasons for the increased water resistance. Proteins are easier to insolubilize because they are inherently less soluble than starches. They are much larger molecular structures with fewer hydrophilic sites. As with starches, protein coatings require a cure period to develop maximum water resistance. Proteins are affected by the same combination of resin concentration, formaldehyde-urea ratio, pH, and temperature.[13]

Melamine-Formaldehyde:

Another commonly used insolubilizing agent is melamine-formaldehyde. Literature examining its use include several patents[6,14-16] and studies.[10,11] In general it is a more efficient means of producing water resistance than urea-formaldehyde. This is due to the six amino groups contained in melamine as opposed to only two in urea. The additional amino groups allow melamine to combine with as many as six formaldehyde molecules. The probable mechanism of reaction for melamine-formaldehyde is the same as for urea-formaldehyde. Crosslinking and blocking of water reactive sites on the adhesive molecules contribute to the increased water resistance. In a coating application the added formaldehyde in melamine-formaldehyde reacts to form a more complex crosslinking network. This accounts for the higher degree of insolubilization attainable with melamine-formaldehyde.[17]

Besides their more efficient production of water resistance, melamine-formaldehydes offer several other advantages. It cures more quickly and under less extreme conditions of pH and temperature. Melamine resins are more heat and light stable than urea resins.

Finally, melamine-formaldehyde does not exhibit the viscosity increase with protein that is characteristic of urea-formaldehyde. This is probably due to the lower concentration of free formaldehyde.[17]

The reaction between melamine-formaldehyde and starch is thought to be the same as that for urea-formaldehyde. A methylol group on the resin combines with a hydroxyl on the starch (α-glucoside). A water molecule is split off. The reaction is shown in Figure 2. In proteins the methylol group is thought to react with an amino group. This reaction is shown in Figure 3. In both cases the insolubilization is accomplished by a combination of crosslinking and blocking of hydrophilic sites. The crosslinking results in large insoluble agglomerates while blocking reduces the water sensitivity of these adhesives. As in urea-formaldehyde, the degree of insolubilization is influenced by the level of addition, resin concentration, temperature, pH, and use of acid catalysts.[10]

Glyoxal:

Glyoxal is a highly reactive dialdehyde. It is frequently used to improve the water resistance of coatings.[11,18-20] As with the formaldehyde derivatives, glyoxal promotes water resistance through the formation of a crosslinked network. Unlike the formaldehyde derivatives, glyoxal requires very little time to cure. In many cases the time required to dry the coating is sufficient. This may be the result of its difunctionality. Glyoxal is most effective under slightly acidic conditions. If made alkaline, glyoxal undergoes an internal Cannizzaro reaction which slowly forms salts of glycolic acid (see Figure 4). In coating situations a pH of 6 to 8 is satisfactory. Reaction with the coating adhesive will occur much more rapidly than the Cannizzaro reaction in this pH range. Acid catalysts may also be used to improve the effectiveness of glyoxal. Magnesium silicofluoride, ammonium sulfonate, and ammonium chloride are commonly used. Care should be taken since these catalysts may lead to undesireable viscosity increases.[20]

Reaction of Starch with Melamine-Formaldehyde
Figure 2
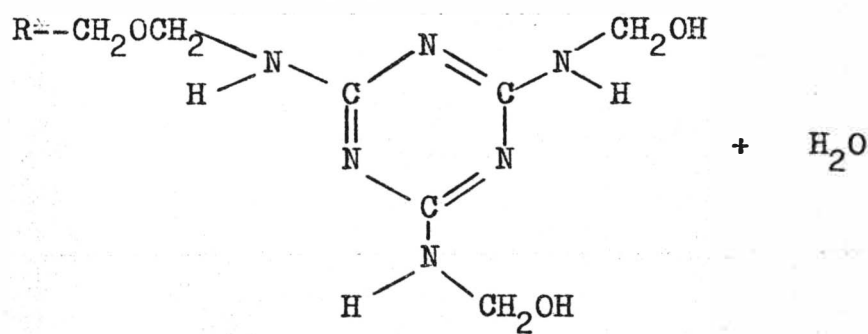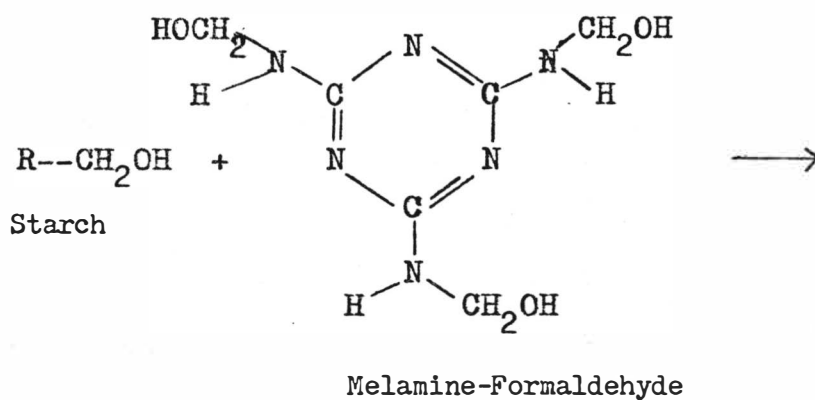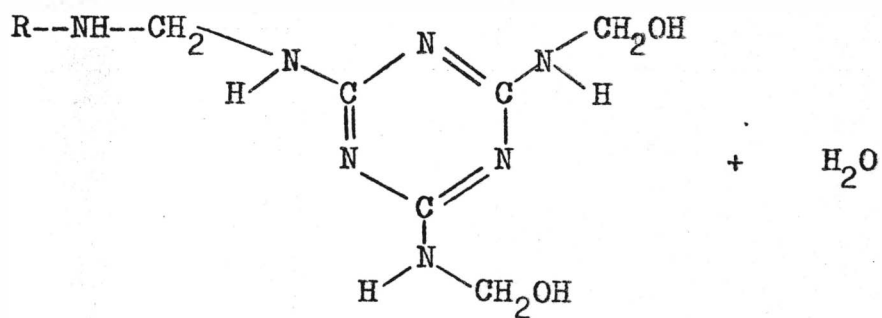
HOCH$_2$—N—C ... N ... C—N—CH$_2$OH (Melamine-Formaldehyde ring structure)

R—CH$_2$OH   +   [Melamine-Formaldehyde structure] $\longrightarrow$

Starch

Melamine-Formaldehyde

R—CH$_2$OCH$_2$—N—C ... N ... C—N—CH$_2$OH (Starch Melamine-Formaldehyde product ring structure)   +   H$_2$O

Starch Melamine-Formaldehyde Product

Reaction of Protein with Melamine-Formaldehyde

Figure 3

R--NH$_2$ +

Protein

Melamine-Formaldehyde

$\longrightarrow$

Protein Melamine-Formaldehyde Product

+   H$_2$O

Glyoxal

Figure 4

$$HO\text{--}C\text{-}H \quad \overset{O}{\underset{O}{C}}\text{--}H \quad H\text{--}\overset{O}{\underset{O}{C}}\text{--}OH$$

$$HO\text{--}C\text{--}H \quad C\text{--}H \quad H\text{--}C\text{--}OH$$

Hydrated Form

$$\begin{array}{c} H\text{--}C\text{==}O \\ | \\ H\text{--}C\text{==}O \end{array}$$

Anhydrous Form

$$\begin{array}{c} H\text{--}C\text{==}O \\ | \\ H\text{--}C\text{==}O \end{array} \quad + \quad OH^- \quad \longrightarrow \quad \begin{array}{c} CH_2OH \\ | \\ COO^- \end{array}$$
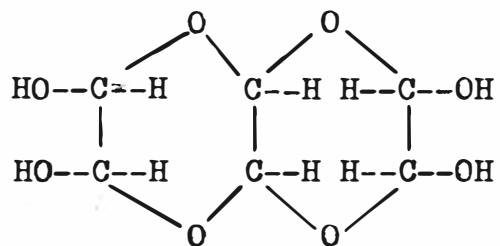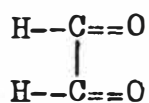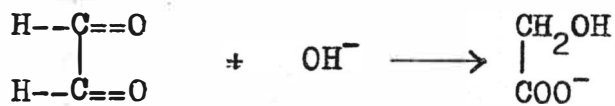
Cannizzaro Reaction in Glyoxal

Glyoxal contributes to crosslinking of starch through a two stage mechanism. In the first stage, while water is still present in the coating, unstable hemi-acetals are formed. As the water is removed during the drying process the hemi-acetals are converted to more stable acetals. Four factors are important to the development of wet resistance with glyoxal. They include the concentration of glyoxal, the drying time, and pH or use of acid catalysts. Another important consideration is the type of starch used. Hydroxyethylated starches have been shown to be the most reactive while dextrins are the least reactive. The point of addition also affects the performance of glyoxal in starch coatings. Buttrick, Kelly, and Eldred[19] indicate that cooking starch at high solids in the presence of glyoxal and utilizing a high percentage of starch in the final coating gave the best results.[11,20]

Glyoxal can also be used in protein coatings. Here it reacts similar to formaldehyde resins and contributes to water resistance in much the same way. When used with protein coatings, glyoxal may contribute to undesireable brightness reversion. In recent years the production of a stabilized glyoxal solution has reduced this possibility.

Eldred and Spicer[21] noted that with the internal application of glyoxal to improve sheet wet strength, the resistance to water was limited to several minutes. Beyond this time the wet strength of the sheet quickly deteriorated. It could not be determined from the literature what effect this may have in coating applications.

Ammonium Zirconium Carbonate:

The use of ammonium zirconium carbonate (AZC) as an insolubilizing agent for offset coatings is not well established in the literature, certainly not as well established as the previously mentioned agents. Its use has been covered by several patents[22-24] but is relatively unsubstantiated. Its chemistry makes it ideal as an insolubilizing agent. Zirconium compounds have a strong affinity for

for oxygen and nitrogen containing groups. In solution they are
polymeric by nature. This is explainable by examining the chemical
nature of zirconium. A valency of 4 and small ionic radius (0.74 A)
tends to make it hydrolyse strongly in water solutions. The hydro-
lysed species are then polymerized. Due to zirconium's high coor-
dination number (8), these polymers can become large. The reactions
that take place between zirconium and an adhesive system is then
dependent upon the affinity for zirconium of the functional groups
on the adhesive as compared to the ions present on the zirconium
compound. Table I lists those functional groups with a strong affinity
for zirconium.

Table I

Functional Groups with Strong Affinities for Zirconium

Mono and Dicarboxylic Acids	R--$\overset{\text{O}}{\underset{\text{}}{C}}$-OH	HO-$\overset{\text{O}}{\underset{\text{}}{C}}$-R--R-$\overset{\text{O}}{\underset{\text{}}{C}}$-OH
Hydroxycarboxylic Acids	HO-R--COOH	
Hydroxyl Ions	OH⁻	
Carbonate Ions	CO_3^-	
Diols	$\overset{R---R}{\underset{HO\quad OH}{\;}}$	

In addition to these groups, the amino groups present in proteins
may also react with zirconium.[25]

Under the conditions generally prevalent in coating systems
(pH 6-11) the compound ammonium zirconium carbonate has been found
to be the most successful insolubilizing compound. It is an alkaline
solution containing carbonate ions. The carbonate ions have an aff-
inity for zirconium and thus prevent it from reacting with other
functional groups that may be in solution. Upon drying AZC loses
carbon dioxide and ammonia and reacts by a crosslinking mechanism

with the adhesive. In some binder systems AZC may react by hydrogen bonding in solution. This can cause a viscosity increase but is only noticeable under low shear conditions.[25]

The actual mechanism of reaction between AZC and an adhesive system depends on the functional groups present. In the case of modified starches carboxyl groups are the primary interaction sites. Hydroxyl groups may reinforce the structure. Unmodified starches will react primarily via hydroxyl groups. Proteins seem to interact via carboxyl groups with some reinforcement from amino groups. The degree of crosslinking and ultimately the water resistance developed is dependent on the affinity of the functional groups present for zirconium.[25]

AZC is reputed to have several significant advantages over more conventional insolubilizing agents. One of the most obvious is the lack of cure time. The crosslinking reaction is triggered by the loss of carbon dioxide and ammonia, both of which are driven off during the drying process. Thus a sheet insolubilized with AZC will show maximum water resistance immediately after leaving the dryer section. AZC does not produce as severe a viscosity increase as is noted with the formaldehyde derivatives. It has no adverse affects on optical properties. In general it is stated as being a more cost effective method of insolubilizing starch and protein coatings.[26]

Testing Procedures:

Through the years a wide variety of instruments have been developed to assess the surface strength of paper. The approaches which have been made can be divided into three categories. These include: force simulators, press models, and on-press testing. The force simulators may be further subdivided to include the two major forces present in an offset press. The forces employed are either plucking[27-28] or rubbing.[29-33] The ammount of material removed by these methods is evaluated by weight, optical densitometry or visual methods with these measurements being used to characterize the sample. Press models or printability testers have also flourished. The best known

in the United States is the IGT printability tester.[34] This instrument allows the operator to control the ink film thickness, pressure, and speed used to test the paper. All of these are important variables relating to sheet surface failure. IGT has also developed a procedure for use with wet resistance tests.[35]

The ultimate test for determining the ability of papers to perform adequately under press conditions remains on-press testing. Since the variables involved in operating a printing press are complex to the point that they are not fully understood, on-press testing offers certain advantages over the previously described methods. Until all of the parameters involved in printing can be completely described, any attempt to simulate press operation will probably fall short of its goal. Secondly, since the paper will be run on a printing press its propensity to fail can best be determined by studying it under press conditions.

Experimental Procedures:

The experimental portion of this thesis has been designed to answer three basic questions:
1) The majority of the available literature deals with the insolubilization of starch coatings. What results can be obtained through the use of conventional insolubilizing agents with protein and how do these results compare with those obtained with starch?
2) Little is available in the literature concerning the use of ammonium zirconium carbonate. How does it compare with conventional insolubilizing agents?
3) Many studies have been made concerning individual insolubilizing agents. How do these materials compare in a side by side analysis?

The literature survey indicates that protein coatings can be expected to show superior water resistance. It might also be expected that melamine-formaldehyde will show the greatest development of wet resistance.

Two secondary studies carried out include an analysis of the
coating viscosities and a monitoring of brightness and K & N values.
The viscosity study examined the effect of addition level on
rheological properties. The optical analysis was to assure that
increasing levels of insolubilizing agent did not adversely affect
these properties.

Coatings:

Two basic formulae were utilized in this experimental procedure.
They have been selected to be similar to coatings that may be used
commercially to produce offset grade papers. As such, the adhesive
portion of each formula will contain a portion of styrene-butadiene
latex. This is in addition to either starch or protein. Table II
outlines the basic formula for both the starch and protein coatings.
A more detailed analysis of each coating used can be found in Appendix I.
These coatings were prepared according to the procedures outlined
in Tables III and IV.

Table II

Basic Coating Formulae

Starch Base:

Ingredient	Parts by Dry Weight
Clay, number 1 coating	100.0
Dispersant, TSPP	0.1
Starch, hydroxyethylated	8.0
Latex, styrene-butadiene	8.0

Protein Base:

Ingredient	Parts by Dry Weight
Clay, number 1 coating	100.0
Dispersant, TSPP	0.1
Protein	10.0
Borax, 5% on protein	0.5
Ammonia, 15% on protein	
Latex, styrene-butadiene	6.0

Table III

Starch-Latex Coating Make-Up Procedure

1) Dissolve the TSPP (tetrasodium pyrophosphate) in water in a double walled cooker. The volume between the walls is filled with water.

2) Disperse the clay (Hydrafine by J. M. Huber) using a Cowles Dissolver. Agitate 10 minutes before applying heat.

3) Heat to 110 F (43.3 C) using a gas burner. The heating is done indirectly via the water contained in the double walled cooker. Add the starch (a hydroxyethylated corn starch, Pen Cote by Penick & Ford). Continue to heat to 185 F (85 C) before shutting off the burner. Hold at this temperature for 15 minutes. Covering the cooker will make holding the temperature more convenient as well as minimizing water losses.

4) Cool to 110 F (43.3 C) by flushing the hot water with cold water. Add the styrene-butadiene (Dow latex 620). Agitation is maintained throughout the cooking procedure.

5) Add the desired insolubilizing agent.

Table IV

Protein-Latex Coating Make-Up Procedure

1) Dissove the TSPP in water in a double walled cooker. The volume between the walls is filled with water and will be used to indirectly cook the protein.

2) Disperse the clay (Hydrafine) using a Cowles Dissolver. Agitate 10 minutes before applying heat. The Cowles is used throughout the cooking procedure. Disperse the borax.

3) Begin heating and adding the Pro-Cote (Ralston Purina). At 110 F (43.3 C) or when the viscosity becomes unmanageable add the ammonia.

Table IV continued.

    4) Continue heating to 150 F (65.6 C). Hold at this temperature
       for 20 minutes. Covering the container will make holding
       the temperature easier and will also minimize water losses.

    5) Cool to 120 F (48.9 C) before adding the Dow 620.

    6) Add the desired insolubilizing agent.

Four commercially available insolubilizing agents were used
in this investigation. Parez 608 is a urea-formaldehyde resin
syrup of a moderate degree of condensation. Parez 707 is a methylated
trimethyol melamine resin. Parez 801 is a stabilized glyoxal resin
containing a trace of formaldehyde. All three agents are available
from American Cyanamid. Bacote 20 is a temperature stabilized form
of ammonium zirconium carbonate. It is available in the United States
from Magnesium Elektron, Inc. These crosslinking agents were added
to the coating formulations after the starch and protein were cooked.
Five levels of addition were used. The UF, MF, and glyoxal resins
were added at 5, 7, 9, 11, and 13 percent based on either starch
or protein. The AZC was added at 1, 3, 5, 7, and 9 percent based
on starch or protein. The difference reflects the purported superior
efficiency of AZC. All levels were based on the manufacturers'
suggestions.[26,36-38]

Application and Drying:

A forty-five pound (25 x 38 - 500) base stock was used in this
procedure. Coatings were applied in the lab using a hand-held blade
drawdown technique. The desired coat weight was four pounds. Coat
weight was checked for each sheet to maintain uniformity. The accept-
able range was established as 3.8-4.2 pounds. This was to minimize
the influence of coat weight during the testing stage.

It was recognized that the method used to dry coated sheets in
the lab would not be representative of a mill application. It was
also recognized that duration and temperature would affect curing

of the insolubilizers. For these reasons drying conditions were standardized. A drying time of 20 seconds at a temperature of 220 F (104.4 C) in a convection oven was used. Selection of these conditions was based on a study made by Dow Chemical Company. Dow has found these conditions to be representative of typical conditions on their pilot coater. Conditions on this pilot coater are similar to those expected on a production blade coater.[39]

All samples were calendered to improve the uniformity of the sheet surface. The usual method utilized a steel to steel calender. Pressure was set using a torque wrench. Sample sheets were treated to two nips. During the course of the coating the steel calender was dismantled to permit regrinding of the rolls. Coatings applied during this period (starch-latex with MF and starch-latex with AZC) received a cold supercalender treatment, 2 nips at 15 psig. It was not felt that this difference would significantly affect the results.

Testing Procedures:

An on-press testing technique was used to determine the water resistance of the coatings being analyzed. (During the initial stages of the investigation the IGT wet pick procedure was attempted. Its shortcomings are summarized in Appendix II.) In all cases the samples used were aged under TAPPI standard conditions for at least two months before testing. This should assure that all resins approached the maximum cure stage. The following procedure was used:

Instrument: AM model 1250 offset printing press
with a standard blue blanket.

Sample Preparation
1) Test strips were cut 1 inch by 5 inches in the machine direction.
2) Five strips at a time were mounted on a press clean up blotter.
3) Successive tests were run, rotating the position of the samples as indicated in Figure 5. This method was

adopted to minimize the variations across the width
of the press.

Testing

1) A blank blotter was placed in the plate clamps. The
fountain solution was set for maximum flow and the
impression set at approximately 60 cycles/minute.
The press was allowed to run 15 minutes to stabilize
and to assure that the flow of fountain solution had
reached equilibrium.

2) The blank blotter was replaced with one containing 5
strips. The press was allowed to run through a pre-
determined number of cycles. The number of cycles is
dependent on the degree of insolubilization.

3) The press was stopped and the blanket allowed 30 seconds
to dry. The piling or linting was examined and each
strip was rated on a scale of from 1 to 5 with 1 being
the best.

4) After cleaning the blanket the test procedure was repeated.
Tests were run in sets with each set containing 5 samples.
The test was repeated 5 times for each set to assure
that each sample occupied each press position (see Figure
5).

5) At the end of the testing, individual ratings were compiled.
The lowest score indicates the highest degree of insol-
ubilization.

Clean-Up

1) Between individual runs the blanket was cleaned with
a solution of isopropyl alcohol and water (50/50 by
volume).

2) Between sets the blanket was cleaned with the alcohol
solution then allowed to dry. After drying it was cleaned
with A. B. Dick blanket cleaner (4-1235) followed by
a second treatment of alcohol solution.

Rotation of Samples for On-Press Testing

Figure 5
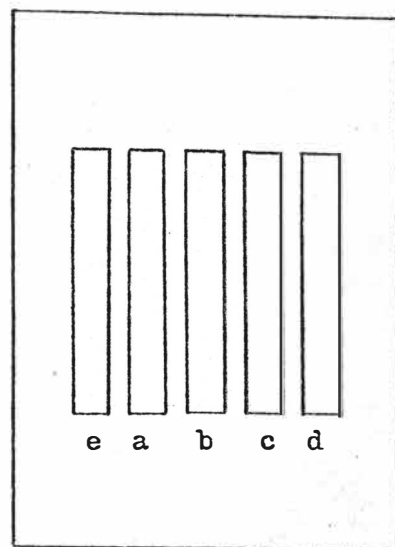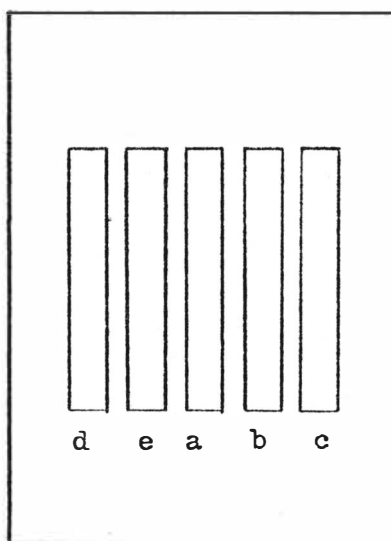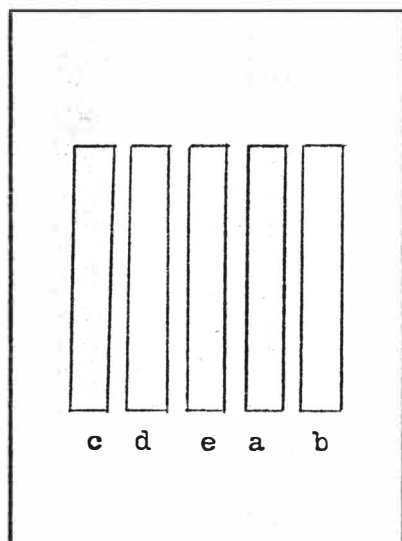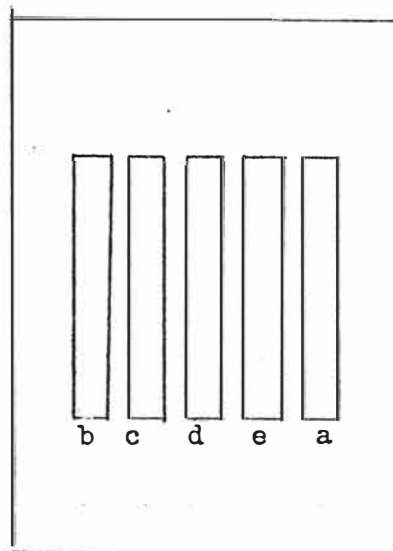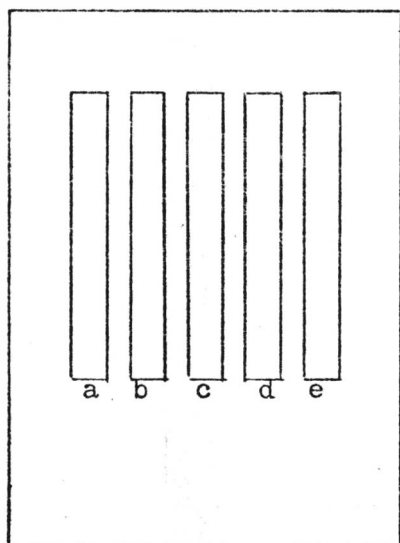
The fountain solution used was made up using 10 ml/liter with distilled water. The final pH was 6.5. For use with the protein coated samples a fountain solution with a pH of 3.5 was made.

Coating viscosities were checked using a Brookfield viscometer at 20 and 100 rpm. The temperature was maintained near 95 F (35 C). These tests were performed immediately after completion of the coating make-up process. Spot checks of G. E. Brightness and K & N value were performed on the coated samples one day and thirty days after coating.

Results:

The data obtained from the on-press wet resistance tests of the starch-latex coated samples is presented in Table V. This is graphically represented in Figure 6. Figure 6 is broken into five sets, representing the five levels of insolubilizing agent used in this investigation. The histograms indicate the relative ranking of UF, MF, glyoxal, and AZC as compared to the starch-latex control.

No data is presented for the protein-latex coatings. The tests performed on these samples proved to be inconclusive. The test did not appear to be severe enough to obtain any meaningful wet resistance results.

The viscosity data obtained from the coatings is presented in Table VI. Viscosity data from both starch-latex and protein-latex coatings is presented here. It is represented graphically in Figures 7 and 8. These figures show viscosity as a function of addition level.

Analysis of brightness and K & N value showed no significant change over the thirty day curing period alloted. The data obtained did not seem to warrant presentation.

Discussion of Results:

Starch-Latex Coatings:

The histograms clearly demonstrate that urea-formaldehyde

Table V

On-Press Wet Resistance Test Results

Starch-Latex Coatings

Level 1	Control	UF	MF	Glyoxal	AZC
	4	1	3	2	5
	4	1	3	2	5
	3	1	2	4	5
	2	4	1	3	5
	4	1	3	5	2
total	17	8	12	16	22
Level 2	4	1	2	5	3
	2	1	3	5	4
	4	1	2	3	5
	3	1	4	2	5
	1	2	3	5	4
total	14	6	14	20	21
Level 3	4	1	2	5	3
	4	1	2	5	3
	3	1	4	2	5
	2.5	1	4	2.5	5
	2	1	3	4	5
total	15.5	5	15	18.5	21
Level 4	2	1	5	4	3
	4	1	2	5	3
	5	2	1	4	3
	4	1	2	5	3
	4	1	2.5	5	2.5
total	19	6	12.5	23	14.5
Level 5	3	2	1	5	4
	4	1	2	5	3
	4	1	2	5	3
	4	1	3	5	2
	4	1	3	5	2
total	19	6	11	25	14

produced the highest degree of insolubilization. This is indicated
by the fact that it consistently has the shortest bar. Since each
bar is generated by a series of five tests, the lowest possible score
is five if that particular sample proved to be the best sample in

Relative Ranking of the Insolubilizing Action
of UF, MF, Glyoxal, AZC
in Starch-Latex Based Coatings
Figure 6

A-- Starch-Latex Control
B-- Urea-Formaldehyde
C-- Melamine-Formaldehyde
D-- Glyoxal
E-- Ammonium Zirconium
      Carbonate

Level 1
Level 2
Level 3
Level 4
Level 5
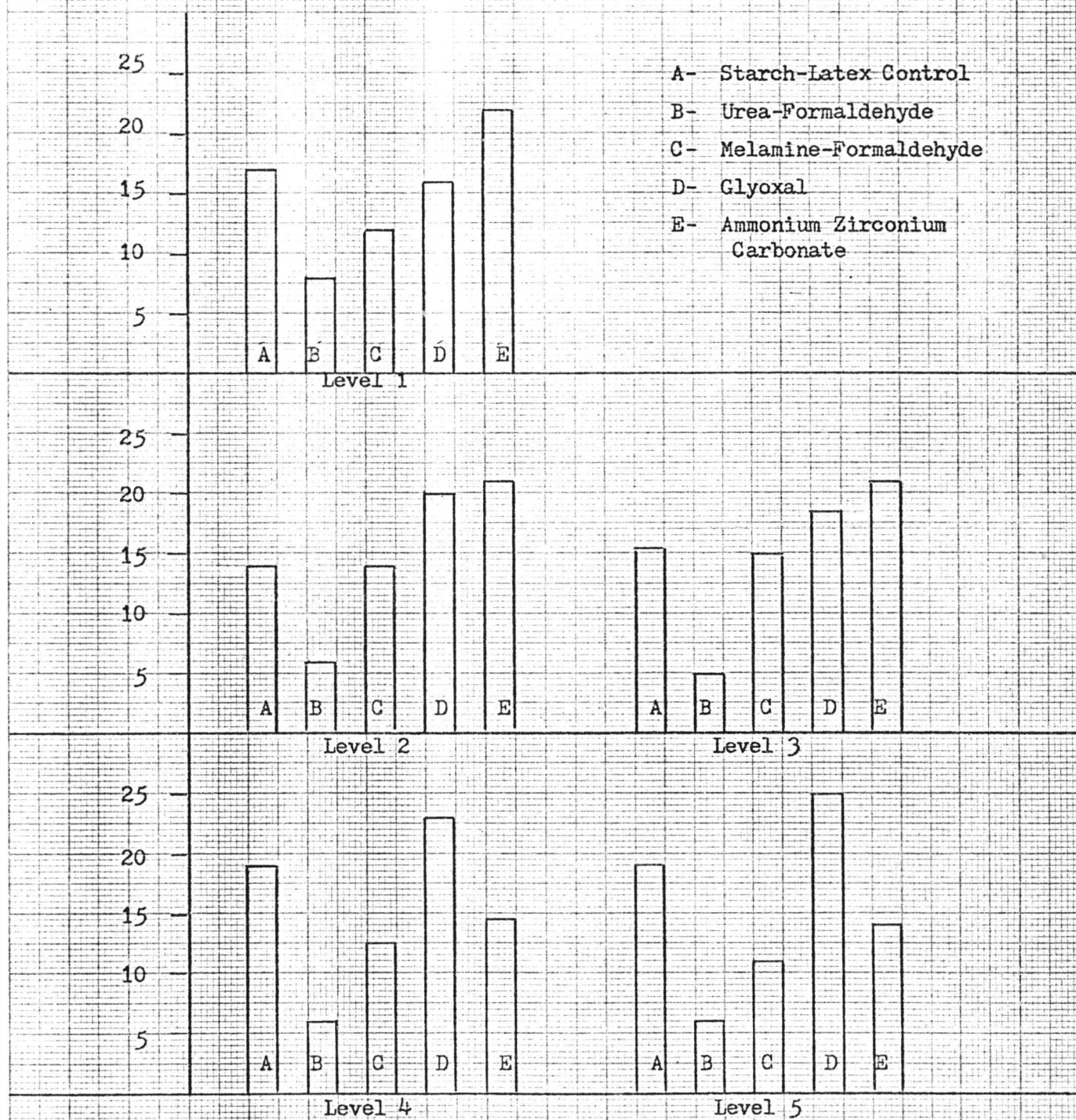
Table VI

Viscosity Data

	Starch-Latex		Protein-Latex	
	20rpm	100rpm	20rpm	100rpm
Control	4840 cP	1292 cP	2120 cP	866 cP
UF 5%	5440 cP	1514 cP	2360 cP	1006 cP
7%	6550	1802	2330	984
9%	6850	1930	2940	1200
11%	6510	1878	3550	1388
13%	7560	2000+	3700	1430
MF 5%	5150 cP	1412 cP	2120 cP	882 cP
7%	5480	1514	2380	984
9%	3580	1000	2200	936
11%	6000	1650	2250	910
13%	5610	1550	2250	894
Gly 5%	5050 cP	1354 cP	5430 cP	1870 cP
7%	5100	1430	5650	1890
9%	4760	1348	5900	1968
11%	4140	1138	8000	2516
13%	4540	1232	7340	2356
AZC 1%	3230 cP	880 cP	2560 cP	1040 cP
3%	3070	860	2810	1090
5%	3420	980	2280	932
7%	3610	1070	2450	1032
9%	4100	1260	2000	882

each test. Urea-formaldehyde was consistently either the best or second best sample. The fact that urea-formaldehyde did score so well proves its superiority over the other insolubilizing agents.

Figure 7 — Starch-Latex Viscosity as a Function of Addition Level

△ UF   ○ Glyoxal
□ MF   ○ AZC   Starch-Latex Control — — —
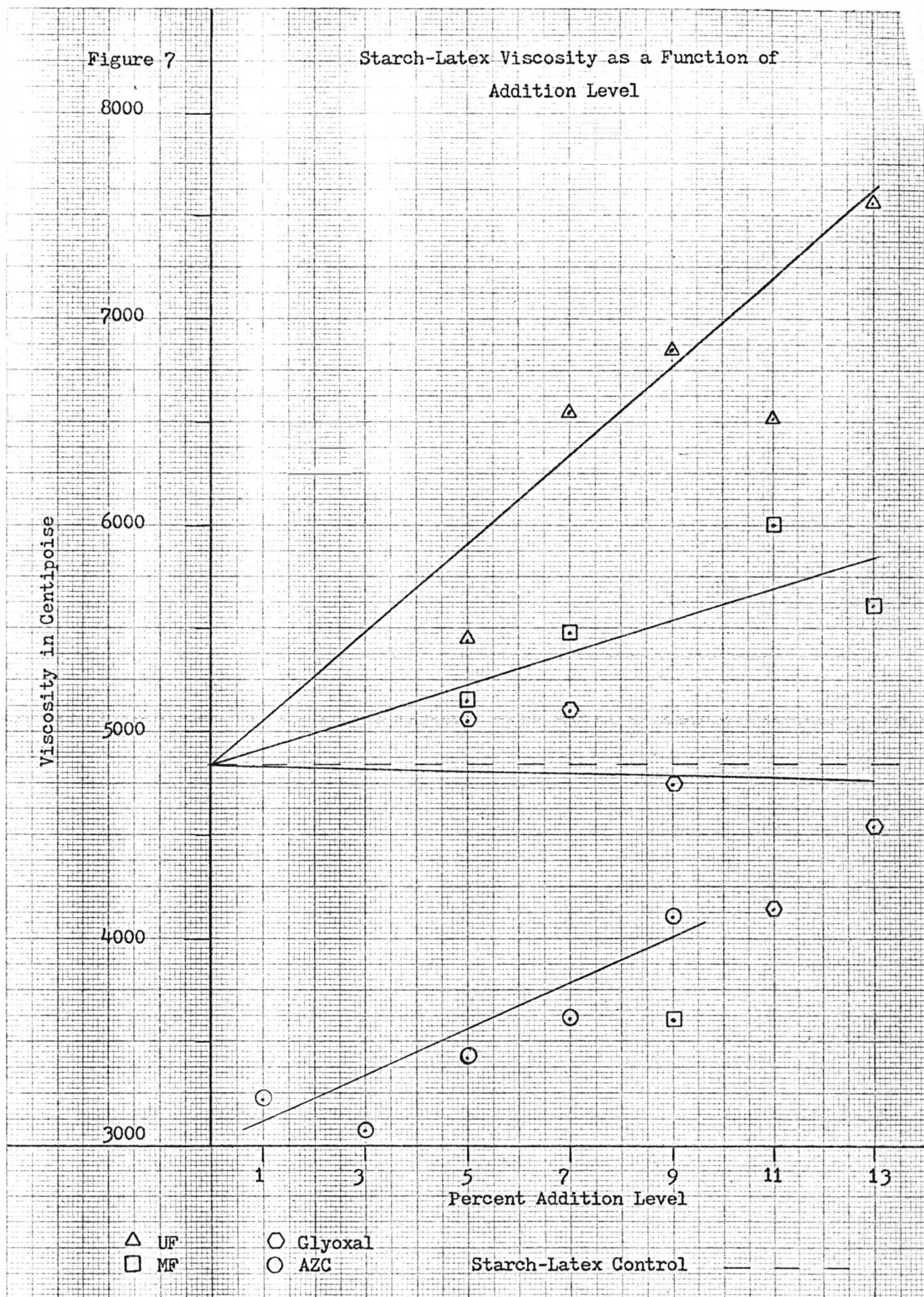
Figure 8

Protein-Latex Viscosity as a Function of
Addition Level

Viscosity in Centipoise

8000

7000

6000

5000

4000

3000

2000

1   3   5   7   9   11   13

Percent Addition Level

△ UF   ⬡ Glyoxal
□ MF   ○ AZC   Protein-Latex Control — — —
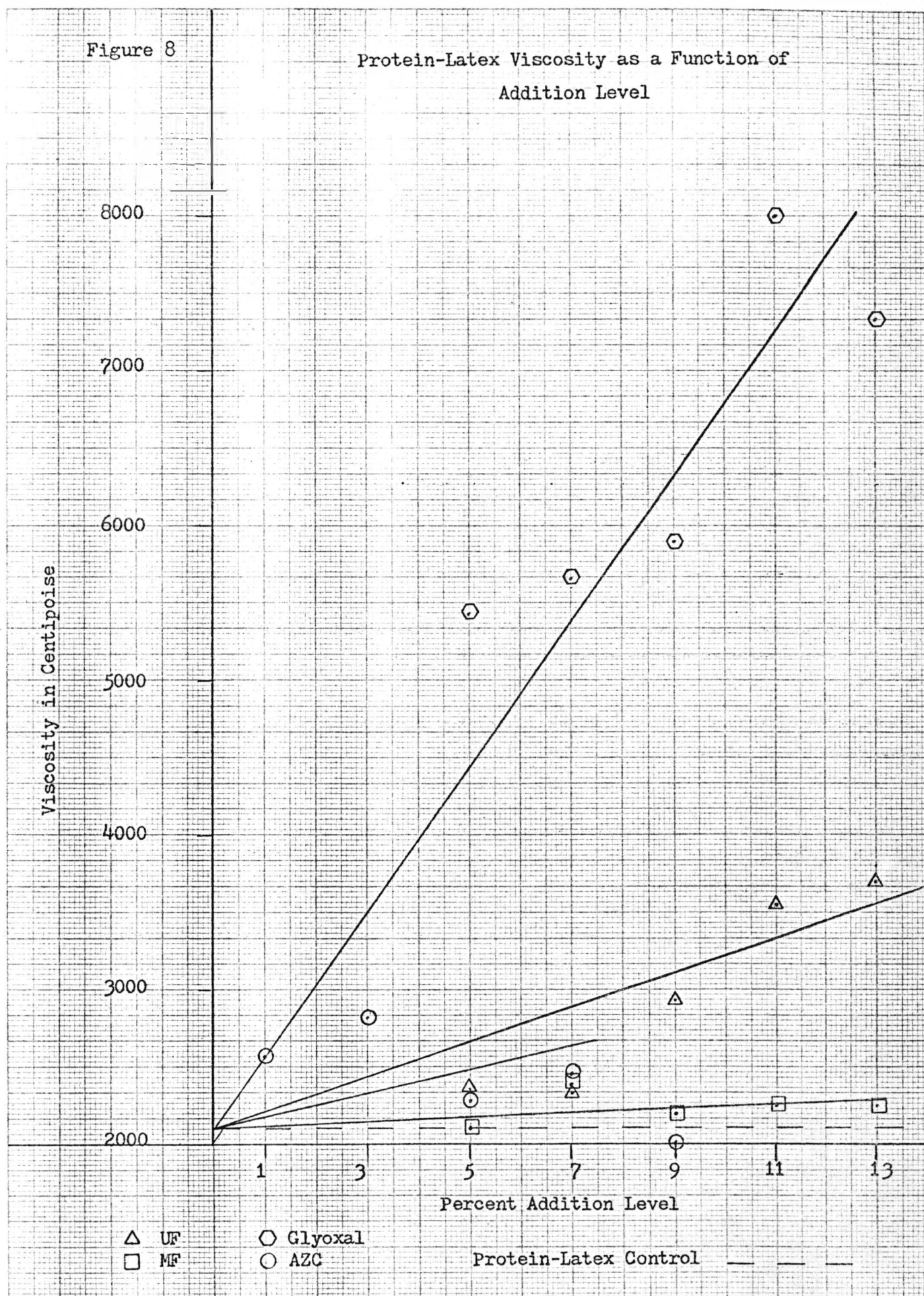
The data indicates that glyoxal harms the water resistance of
starch-latex coatings. At all but the lowest addition level (5%)
glyoxal shows water resistance inferior to the control coating.
A weak trend seems to exist toward an increasing disparity between
the control and the glyoxal samples. If this is actually the case
it would indicate that increasing levels of glyoxal further reduce
the wet resistance of starch-latex coatings. It has been suggested
that this may be due to the latex present in the coating. Buttrick,
Kelly, and Eldred[19] have indicated that glyoxal is most effective
with the highest possible starch concentration in the adhesive.
The presence of latex will lower this concentration and detract from
the glyoxal efficiency.

When compared with the control coating, AZC shows a definite
improving trend. At the three lowest levels of addition (1, 3, and
5 percent) it shows less water resistance than the control, but each
time by a narrower margin. The improvement continues in the 7 and
9 percent levels. At these levels it is only slightly worse than
melamine-formaldehyde. It must be remembered, however, that the
melamine-formaldehyde samples used for comparison here contain 11
and 13 percent crosslinking agent. This substantiates the proposal
that AZC is a more efficient insolubilizing agent.

Examining the histograms, as addition level is increased there
is an increasing disparity between the control and the UF, MF, and
AZC samples. The control clearly becomes consistently worse. This
indicates an increased degree of insolubilization with increased
level of addition. Glyoxal, as has been mentioned before, seems
to become worse with increased level of addition.

Protein-Latex Coatings:

Wet resistance tests were run on the protein-latex coated samples
using the same on-press test procedure used for the starch-latex
coatings. Initially a fountain solution with a pH of 6.5 was tried.
The coating did not fail even after being subjected to 150 cycles.

(Failure was noted by observing piling on the blanket. In the case of the starch-latex coatings, this occured within 50 cycles.) A second fountain solution with a pH of 3.5 was tried. It was thought that the more acidic fountain solution would provide a more severe test. Once more, there was no failure even after 200 cycles. Since the control coating did not fail either, any evaluation of these insolubilizing agents in protein-latex coatings by the methods used here must be considered inconclusive.

Viscosity and Optical Tests:

The viscosity data collected during the coating make-up procedure for starch-latex colors indicates the following trends. Both UF and MF showed distinct viscosity increases with increased addition levels. UF showed the most dramatic increase. The viscosity of the glyoxal coatings remained relatively constant. There may have been a slight downward trend but this was not significant. Initially AZC showed a dramatic viscosity drop as compared to the starch-latex control. This was followed by a slight increasing trend as the addition level was increased. The viscosity of the highest addition level did not approach that of the control. This unexpected behavior has not been explained.

The data collected for the protein-latex coating viscosities showed the following trends. UF, MF, and glyoxal all showed viscosity increases with increased addition levels. Glyoxal showed the most dramatic increase, while MF actually remained quite stable. The UF coatings were intermediate. AZC showed a downward trend with increased addition levels.

Brightness and K & N values were examined for all coatings one and 30 days after coating application. No significant differences were found either with aging, addition level variation, or between the various crosslinking agents.

Conclusions:

The following conclusions may be drawn relating to the use of

urea-formaldehyde, melamine-formaldehyde, glyoxal, and ammonium
zirconium carbonate in offset coatings under the conditions set
up for this thesis.

Starch-Latex Coatings:

1) Urea-formaldehyde showed superior development of water
   resistance at all levels of addition. This was accom-
   panied by a sharp viscosity increase in the coating.

2) Addition of glyoxal impared the development of water
   resistance. Increasing levels of addition were progres-
   sively more harmful. Glyoxal had little affect on the
   viscosity of starch-latex coatings.

3) Above a level of 5 percent, ammonium zirconium carbon-
   ate was competitive with more conventional insolubilizing
   agents, even when the conventional agents were added
   at significantly higher levels. Ammonium zirconium
   carbonate reduced starch-latex coating viscosities.

4) The degree of insolubilization increased with increased
   addition level for UF, MF, and AZC.

5) All four agents showed no significant affect on bright-
   ness or K & N value.

Protein-Latex Coatings:

1) Protein-latex coatings developed a degree of water
   resistance significantly higher than starch-latex
   coatings.

2) Under the conditions of this thesis, a relative ranking
   of the insolubilizing agents used is not possible.

Recommendations:

Several areas related to this thesis remain to be investigated.
The most obvious of these concerns the use of insolubilizing agents
in protein based coatings. The protein-latex coatings analyzed in

this thesis yielded an inconclusive comparison of the insolubilizing agents under study. Future studies could take two directions. The first may be to eliminate the use of a latex in combination with protein. Thsi should lower the water resistance of the coatings and make a comparative analysis possible. A second direction would be to increase the severity of the test sufficiently to cause the coatings to fail.

Initially a curing rate study was planned for this thesis. Complications resulted in its being eliminated. This is another area of investigationopen to further study. It is known that cure rates of some of the resins used in this study are significantly altered by the use of catalysts and heat. An evaluation with respect to these variables could prove particularly beneficial.

The on-press test procedure used in this thesis provides at best a qualitative analysis of the coatings under study. A very profitable area of study involves the refinement of this test pro-cedure. The work of Daniels[1] suggests that on-press testing has great potential as a research tool for analyzing the behavior of offset papers and coatings. His work develops a method of on-press testing capable of arriving at a quantitative single number evaluation of the linting properties of paper. This test may be easily applied to water resistance tests.

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51. "Wet Rub of Coated Papers (Wet Finger)," Tappi Routine Control Method, RC-185.

Appendix I

The following is a list of the formulae used to produce the starch-latex and protein-latex coatings analyzed in this thesis.

Starch-Latex Coatings:

	Ingredient	Wet Weight	% Solids	Dry Weight
Control	Water	325.4	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Latex	74.4	50	37.2
		906.7	60	544.0
	actual solids		60.0	

Clay-- no. 1 coating grade, Hydrafine J.M. Huber
Starch-- hydroxyethylated corn, Pen-Cote Penick & Ford
Latex-- styrene-butadiene, Dow Latex 620 Dow Chemical

UF 5%	Water	325.7	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Parez 608	2.82	66	1.86
	Latex	74.4	50	37.2
		909.8	60	545.9
	actual solids		59.4	

UF 7%	Water	325.8	--	---
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	ЭtStarch	37.2	100	37.2
	Parez 608	3.94	166	2.60
	Latex	74.4	50	37.2
		911.0	60	546.6
	actual solids		59.3	

UF 9%	Water	326.0	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Parez 608	5.08	66	3.35
	Latex	74.4	50	37.2
		912.3	60	547.4
	actual solids		59.9	

		Ingredient	Wet Weight	% Solids	Dry Weight
UF	11%	Water	326.2	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 608	6.20	66	4.09
		Latex	74.4	50	37.2
			913.6	60	548.1
		actual solids		60.1	
UF	13%	Water	326.2	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 608	7.3	66	4.84
		Latex	74.4	50	37.2
			914.8	60	548.9
		actual solids		59.3	
MF	5%	Water	326.3	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 707	2.33	80	1.86
		Latex	74.4	50	37.2
			909.8	60	545.9
		actual solids		59.3	
MF	7%	Water	326.6	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 707	3.25	80	2.60
		Latex	74.4	50	37.2
			911.1	60	546.6
		actual solids		59.4	
MF	9%	Water	326.7	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 707	4.19	80	3.35
		Latex	74.4	50	37.2
			912.3	60	547.4
		actual solids		60.3	

		Ingredient	Wet Weight	% Solids	Dry Weight
MF	11%	Water	327.2	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 707	5.11	80	4.09
		Latex	74.4	50	37.2
			913.6	60	548.1
		actual solids		60.0	
MF	13%	Water	327.5	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 707	6.05	80	4.84
		Latex	74.4	50	37.2
			914.8	60	548.9
		actual solids		58.9	
Glyoxal	5%	Water	323.9	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 801	4.65	40	1.86
		Latex	74.4	50	37.2
			909.8	60	545.9
		actual solids		60.7	
Glyoxal	7%	Water	323.2	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 801	6.5	40	2.60
		Latex	74.4	50	37.2
			911.0	60	546.6
		actual solids		60.7	
Glyoxal	9%	Water	322.7	--	--
		TSPP	4.65	100	4.65
		Clay	465.0	100	465.0
		Starch	37.2	100	37.2
		Parez 801	8.38	40	3.35
		Latex	74.4	50	37.2
			912.3	60	547.4
		actual solids		60.9	

	Ingredient	Wet Weight	% Solids	Dry Weight
Glyoxal 11%	Water	322.0	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Parez 801	10.22	40	4.09
	Latex	74.4	50	37.2
		913.5	60	548.1
	actual solids		60.0	
Glyoxal 13%	Water	321.4	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Parez 801	12.1	40	4.84
	Latex	74.4	50	37.2
		914.8	60	548.9
	actual solids		60.0	
AZC 1%	Water	324.9	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Bacote 20	1.24	30	0.372
	Latex	74.4	50	37.2
		907.4	60	544.4
	actual solids		60.1	
AZC 3%	Water	323.6	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Bacote 20	3.72	30	1.12
	Latex	74.4	50	37.2
		908.6	60	545.2
	actual solids		59.2	
AZC 5%	Water	322.4	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Bacote 20	6.2	30	1.86
	Latex	74.4	50	37.2
		909.8	60	545.9
	actual solids		59.5	

	Ingredient	Wet Weight	% Solids	Dry Weight
AZC 7%	Water	321.1	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Bacote 20	8.67	30	2.60
	Latex	74.4	50	37.2
		911.0	60	546.6
	actual solids		59.5	
AZC 9%	Water	319.9	--	--
	TSPP	4.65	100	4.65
	Clay	465.0	100	465.0
	Starch	37.2	100	37.2
	Bacote 20	11.17	30	3.35
	Latex	74.4	50	37.2
		912.3	60	547.4
	actual solids		59.2	

Protein-Latex Coatings:

	Ingredient	Wet Weight	% Solids	Dry Weight
Control	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	170.4	--	--
	Ammonia	6.0	--	--
	Latex	48.0	50	24.0
		870.4	54	470
	actual solids		53.6	

Clay-- no. 1 coating grade, Hydrafine J.M. Huber
Protein-- Pro-Cote MV Ralston Purina
Latex-- styrene-butadiene, Dow Latex 620 Dow Chemical

	Ingredient	Wet Weight	% Solids	Dry Weight
UF 5%	Water	200.0	--	--
	TSPP	4.65	100	4.65
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	171.1	--	--
	Ammonia	6.0	--	--
	Parez 608	3.03	66	2.00
	Latex	48.0	50	24.0
		874.1	54	472
	actual solids		54.3	

	Ingredient	Wet Weight	% Solids	Dry Weight
UF 7%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	171.4	--	--
	Ammonia	6.0	--	--
	Parez 608	4.24	66	2.80
	Latex	48.0	50	24.0
		875.6	54	472.8
	actual solids		54.2	
UF 9%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	171.6	--	--
	Ammonia	6.0	--	--
	Parez 608	5.45	66	3.60
	Latex	48.0	50	24.0
		877.0	54	473.6
	actual solids		54.4	
UF 11%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	171.8	--	--
	Ammonia	6.0	--	--
	Parez 608	6.67	66	4.40
	Latex	48.0	50	24.0
		878.5	54	474.4
	actual solids		54.1	
UF 13%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	172.1	--	--
	Ammonia	6.0	--	--
	Parez 608	7.88	66	5.20
	Latex	48.0	50	24.0
		880.0	54	475.2
	actual solids		53.5	

	Ingredient	Wet Weight	% Solids	Dry Weight
MF 5%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	171.6	--	--
	Ammonia	6.0	--	--
	Parez 707	2.50	80	2.00
	Latex	48.0	50	24.0
		874.1	54	472.0
	actual solids		53.4	
MF 7%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	172.1	--	--
	Ammonia	6.0	--	--
	Parez 707	3.50	80	2.80
	Latex	48.0	50	24.0
		875.6	54	472.8
	actual solids		54.2	
MF 9%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	172.5	--	--
	Ammonia	6.0	--	--
	Parez 707	4.50	80	3.60
	Latex	48.0	50	24.0
		877.0	54	473.6
	actual solids		54.1	
MF 11%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	173.0	--	--
	Ammonia	6.0	--	--
	Parez 707	5.50	80	4.40
	Latex	48.0	50	24.0
		878.5	54	474.4
	actual solids		54.0	

	Ingredient	Wet Weight	% Solids	Dry Weight
MF 13%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	173.5	--	--
	Ammonia	6.0	--	--
	Parez 707	6.5	80	5.20
	Latex	48.0	50	24.0
		880.0	54	475.2
	actual solids		54.6	
Glyoxal 5%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	169.1	--	--
	Ammonia	6.0	--	--
	Parez 801	5.00	40	2.00
	Latex	48.0	50	24.0
		874.1	54	472.0
	actual solids		54.6	
Glyoxal 7%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	168.6	--	--
	Ammonia	6.0	--	--
	Parez 801	7.00	40	2.80
	Latex	48.0	50	24.0
		875.6	54	472.8
	actual solids		54.1	
Glyoxal 9%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	168.0	--	--
	Ammonia	6.0	--	--
	Parez 801	9.00	40	3.60
	Latex	48.0	50	24.0
		877.0	54	473.6
	actual solids		54.2	

	Ingredient	Wet Weight	% Solids	Dry Weight
Glyoxal 11%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	167.5	--	--
	Ammonia	6.0	--	--
	Parez 801	11.00	40	4.40
	Latex	48.0	50	24.0
		878.5	54	474.4
	actual solids		54.5	
Glyoxal 13%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	167.0	--	--
	Ammonia	6.0	--	--
	Parez 801	13.00	40	5.20
	Latex	48.0	50	24.0
		880.0	54	475.2
	actual solids		54.4	
AZC 1%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	169.8	--	--
	Ammonia	6.0	--	--
	Bacote 20	1.33	30	0.40
	Latex	48.0	50	24.0
		871.1	54	470.4
	actual solids		54.5	
AZC 3%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	168.6	--	--
	Ammonia	6.0	--	--
	Bacote 20	4.00	30	1.20
	Latex	48.0	50	24.0
		872.6	54	471.2
	actual solids		54.8	

	Ingredient	Wet Weight	% Solids	Dry Weight
AZC 5%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	167.4	--	--
	Ammonia	6.0	--	--
	Bacote 20	6.67	30	2.00
	Latex	48.0	50	24.0
		874.1	54	472.0
	actual solids		54.2	
AZC 7%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	166.3	--	--
	Ammonia	6.0	--	--
	Bacote 20	9.33	30	2.80
	Latex	48.0	50	24.0
		875.6	54	472.8
	actual solids		55.0	
AZC 9%	Water	200.0	--	--
	TSPP	4.00	100	4.00
	Clay	400.0	100	400.0
	Borax	2.00	100	2.00
	Protein	40.0	100	40.0
	Water	165.0	--	--
	Ammonia	6.0	--	--
	Bacote 20	12.00	30	3.60
	Latex	48.0	50	24.0
		877.0	54	473.6
	actual solids		54.4	

Appendix II

The original experimental design for this thesis called for
a quantitative analysis of water resistance development. The coatings
were to be analyzed using the method described in IGT information
leaflet W32. Briefly, this method employs the IGT AC2 printability
tester. Both printing disk shafts were to be employed. A rubber
dampening disk was mounted on the top shaft. The dampening disk
was kept moist by a weighted doctor blade enclosing a moisture ladened
cotton wick. An ink roller was mounted on the second shaft. When
running a test the paper sample comes in contact with the dampening
roller first and then with the ink roller. By running the test in
the constant speed mode, both the picking force and the water contact
time can be calculated. The dampening unit has been calibrated to
apply a constant, known ammount of water. The applied ink film thick-
ness is also known by controlling the inking procedure. Thus the
entire printing procedure can be controlled and characterized. Test
results were to be quantitatively determined by measuring the optical
density of the removed coating.

The problem encountered with the method was twofold. At low
pick forces wet repellancy impared observation of wet pick. Since
wet pick could not be singled out from wet repellancy, the use of
an optical density measuring system was precluded. Visual observation
aided by magnification also failed to distinguish coating failure
from wet repellancy. At high pick forces fiber failure occured.
Under dry conditions fiber failure occured before coating failure.
Using the dampening system it was still not possible to distinguish
coating failure well enough to provide the desired comparisons.
For these reasons the IGT method was abandoned in favor of the on-
press method. Time spent working with the IGT method also necces-
sitated abandoning a proposed cure rate study.